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THE GLIDDEN COMPANY, NAVAL STORES DIVISION, JACKSONVILLE. FLORIDA. A STUDY OF THE CHARACTERISTICS OF THE WASTES RESULTING FROM THE DESTRUCTIVE DISTILLATION OF PINE WOOD

Virgil A. Minch, et al

Environmental Health Center
Cincinnati, Ohio

28 February 1952

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INDUSTRIAL WASTE SURVEY REPORT

THE GLIDDEN COMPANY,
NAVAL STORES DIVISION
JACKSONVILLE, FLORIDA

A STUDY OF THE CHARACTERISTICS OF THE WASTES RESULTING FROM THE DESTRUCTIVE DISTILLATION OF PINE WOOD

February 4 to February 28, 1952

FEDERAL SECURITY AGENCY
PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

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Springfield VA 22151

Industrial Waste Survey Report

THE GLIDDEN COMPANY

Naval Stores Division

Jacksonville, Florida

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February 4 to February 28, 1952

A Study of the Characteristics of the Wastes Resulting from the Destructive Distillation of Pine Wood

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A B S T R A C T

This survey was undertaken as part of the U. S. Public Health Service program of industrial waste studies for the purpose of determining volume and characteristics of liquid wastes resulting from various manufacturing processes.

The Jacksonville Naval Stores Division of the Glidden Company operates eight oil-fired retorts to produce charcoal and liquid pine products from seasoned pine wood by destructive distillation. An average of 100 tons of wood are carbonized daily from which 40,000 pounds of charcoal, 4,000 gallons of pine tar, 400 gallons of turpentine, 250 gallons of dipentene, 100 gallons of pine oil, and 250 gallons of low-boiling solvents are produced. The liquid products are generally referred to as "Naval Stores."

The liquid waste directly resulting from the wood pyrolysis is known as pyroligneous acid liquor and is an extremely complex mixture containing at least 35 identifiable organic compounds, many of which are water soluble. It is a dark red-brown liquid having a strong acid reaction and a peculiar empyreumatic odor. The yield of pyroligneous acid liquor from softwood distillation is 50 to 60 per cent of the weight of the wood processed. The volume at this plant amounted to 15,000 gallons per day. This waste has limited uses as a disinfectant, weed killer, and meat curing agent, but probably accounts for less than 2 per cent of the total production. The largest percentage goes to waste.

The only other waste associated with the destructive distillation process is condenser cooling water. The water used in the condensers is pumped directly from artesian wells and discharged without further use to Moncrief Creek. Any pollutants found in the waste are therefore due to condenser

leakage. Leakage was evident from the fact that 5-day B.O.D. values ranged from 4 to 1,740 pounds discharged daily.

Pyroligneous acid liquor was sampled at three points in the plant, but was in effect the same waste with different degrees of treatment. The points sampled were as follows:

1. Raw Pyroligneous Acid Liquor
2. Extracted Pyroligneous Acid Liquor
3. Pyroligneous Acid Liquor from Settling Pond

Raw pyroligneous acid liquor was sampled as it was pumped from the plant to the settling pond, extracted pyroligneous acid liquor was a portion of the same sample after laboratory extraction, and pyroligneous acid liquor from the settling pond was a surface sample after approximately two days retention.

Average values of the various constituents of the wastes and the per cent difference due to extraction and settling are tabulated below:

PYROLIGNEOUS ACID LIQUOR

Constituent - Lbs/Day		Raw	Extracted	Difference Per Cent	Settled	Difference Per Cent
Immediate Oxygen Demand		453	535	* 18.1	145	- 68.0
B.O.D., 5 Day - 20° C.		8,270	8,360	* 1.0	3,920	- 52.6
Oxygen Consumed		17,500	15,500	- 11.4	7,390	- 57.8
Volatile Acids as Acetic Acid		2,990	3,120	* 4.3	1,730	- 42.1
Color		495	590	* 19.1	463	- 6.5
Phenols		247	138	- 44.1	104	- 57.9
Ether Extractable Material		2,780	910	- 67.2	428	- 84.6
Lignin and Tannin as Tannic Acid		8,910	8 580	- 3.7	3,820	- 57.1
Total Solids,	Total	4,940	4,200	- 15.0	2,410	- 51.2
	Volatile	4,720	4,040	- 14.4	2,240	- 52.5
	Fixed	220	160	- 27.3	170	- 22.7
Suspended Solids,	Total	156	4	- 97.4	3	- 98.1
	Volatile	151	4	- 97.4	3	- 98.0
	Fixed	5	0	-100.0	0	-100.0
Dissolved Solids,	Total	4,780	4,200	- 12.1	2,410	- 49.6

* = increase

- = decrease

Results of the extracted waste are based on laboratory extracted samples and are only indicative of what might occur on a full scale plant application. Extraction on a continuous basis was to be initiated by the company at the close of the survey.

GENERAL INFORMATION

1. Organization of Survey

Arrangements for this co-operative project were made by officials of the Florida State Board of Health. The Environmental Health Center of the United States Public Health Service was invited by the Southeast Drainage Basin office to study naval stores wastes. Several conferences were held by personnel of the Florida State Board of Health, Environmental Health Center, and the Glidden Company to discuss results of previous studies, analytical procedures, and the conduct of the survey.

2. Period of Survey

February 4 to February 28, 1952.

3. Personnel

The following personnel participated in the organization and conduct of the survey:

FLORIDA STATE BOARD OF HEALTH
John Wakefield, Sanitary Engineer
William M. Beck, Jr., Biologist

GLIDDEN COMPANY
J. P. Bain, Technical and Research Director
R. E. Fuguitt, Plant Superintendent
A. B. Booth, Research Chemist

UNITED STATES PUBLIC HEALTH SERVICE
H. H. Black, Chief, Industrial Wastes Section
Virgil A. Minch, Assistant Sanitary Engineer
Robert L. Harris, Assistant Sanitary Engineer
William W. Walker, Chemist
Carl N. Shadix, Chemist
Carl R. Hirth, Chemist
Melvin D. Currey, Chauffeur Mechanic

4. Purpose

This survey was conducted to determine source, quantity, concentration, and characteristics of process wastes resulting from the destructive distil-

lation of pine wood. This information will serve as an aid in determining the principal factors influencing the characteristics of destructively distilled wood naval stores wastes. The results of this survey and similar studies will serve as a basis for preparation of an industrial waste guide on wood naval stores plants.

5. Location of Plant

The main offices of the Glidden Company are located in Cleveland, Ohio. The industrial plant, laboratories, and offices of the Jacksonville Naval Stores Division are located adjacent to Moncrief Creek, Duval County, Jacksonville, Florida.

6. Brief History of the Naval Stores Industry in the United States

The term "Naval Stores" is not capable of accurate definition. Originating in the days of wooden sailing ships it included tar, pitch, rosin, turpentine, cordage, masts, and yards. The term still persists today and generally includes all the above-mentioned commodities - except cordage, masts, and yards - with the addition of pine oil, dipentene, other terpene hydrocarbons, and tall oil. The Naval Stores Act of 1923 specifically defines naval stores as spirits of turpentine and rosin.

Seagoing Phoenicians used rosin and tar in the caulking of ships and ships' holds, and for the treatment of rope. Fluid wood tar and pyroligneous acid were used by the ancient Egyptians for embalming their dead. Records show that in 1608 tar, pitch, turpentine, and rosin were made in Virginia and shipped to England. This cargo marked the first recorded shipment of industrial products from America to the Old World.

Today four distinct methods are used in the United States in the production of naval stores;

(a) Steam and solvent extraction of pine stumps
(b) Distillation of crude gum or oleoresin obtained by tapping live trees
(c) The recovery and refining of relief gases and black liquor soap from sulfate pulping of pine wood
(d) Destructive distillation of pine wood in retorts

The original method of production was destructive distillation, called "tar burning," of heartwood in crude sod pits and earthen kilns. For a long time charcoal was the main product although some tar, pitch, and gases were recovered. Later the method of tapping live trees for the exudate was initiated and this procedure is still used to gather crude gum.

Although both these methods of production were developed and expanded, the yield from the tapping of live trees far exceeded that of destructive distillation. New England was the largest producer until the late 1680's when settlers in North Carolina discovered that the southern yellow or long-leaf pine was a more abundant source of gum than the pitch pine of New England. By 1700 the production of gum naval stores was an important part of the economy of North Carolina.

The area of production of gum naval stores has shifted through the years. North Carolina remained the largest producing state for over 150 years, until about 1880 when South Carolina assumed leadership. From 1890 until 1906 Georgia led in production at which time it was superseded by Florida. In 1924 Georgia reclaimed the lead and has retained it to date. The shift in production was brought about by the cutting of virgin forests without leaving seed trees for reproduction. The original pine belt extended from Virginia to Texas and covered an estimated 100,000 square miles of nearly unbroken virgin forest.

In almost 350 years of history there have been few fundamental changes in the original method of gum naval stores production. The most important change

was the development of centralized gum-cleaning plants. As recently as 1935 practically all production was by fire still, and at one time there were about 2500 such stills in operation. Centralized steam distillation has been on the increase until today there are only about 100 fire stills left. In 1948 there were 31 central stills in the southeastern United States, distributed as follows:

Georgia	—	24
Florida	—	5
Alabama	—	2

The products of the gum branch of the industry are gum rosin and gum spirits of turpentine.

Primitive methods of destructive distillation did not take into account the difference in composition of woods. Although the methods of distillation are the same for both "hard" and "soft" woods the resulting products differ somewhat. The products of hardwood distillation are wood gas, pyroligneous acid (from which methenol and acetic acid are recovered), wood tar and charcoal. These products are not generally considered naval stores. In softwood distillation, notably pine, considerable quantities of volatile oils and resinous bodies are recovered. Upon fractionation, pine oil, turpentine, dipentene, pine tar, and terpene solvents are obtained.

The first distillation of wood on a commercial scale in this country was made in 1830 in North Adams, Massachusetts, when James Ward began the manufacture of pyroligneous acid and charcoal. In 1872 James Stanley and associates erected a plant in Wilmington, North Carolina, for the destructive distillation of pine wood. This plant consisted of a series of retorts with attached condensers set up in brickwork with furnaces beneath. The resulting liquid products were not separated and were used for the preservation of timber. With the advent of more efficient equipment this phase of the naval stores industry expanded. Larger

plants were built at Jacksonville and Pensacola, Florida, New Orleans, Louisiana, and Fayetteville, North Carolina. Many smaller plants were built in the Carolinas, Georgia, and Alabama, which are no longer operating. In 1947 there were 19 soft wood destructive distillation plants distributed as follows:

Florida	- 5	Mississippi	- 1
Georgia	- 3	Massachusetts	- 1
Texas	- 3	Vermont	- 1
Ohio	- 2	Washington	- 1
Louisiana	- 2		

The products of this phase of the industry are known as destructively-distilled (D.D.) wood naval stores and include pine tar, pine tar oil, pyroligneous acid, D.D. dipentene, D.D. turpentine, D.D. pine oil, and charcoal.

As early as 1900 the Federal Government urged that new sources of naval stores be found because it was feared that lumbering and poor manufacturing procedures would soon seriously affect production in this country.

A new source of naval stores was discovered in 1905 based upon the experiments of George Walker who recovered volatile oils from pine light wood. A plant was built at Conway, South Carolina, which produced about 200 barrels of rosin per week, and some turpentine. The plant was not a continuing success and soon passed into receivership.

In 1907 Homer T. Yaryan, a native of Indiana, became interested in the value of dead pine stumps. He conceived the idea of grinding the stumps and extracting the essential oils with a solvent. A plant was built at Gulfport, Mississippi, in 1909, embodying the fundamental principles of this phase of the naval stores industry.

Primarily because of engineering research and development the industry flourished, and at present there are fourteen plants operated by nine companies in five southern states. The fourteen plants process more than 2,000,000 tons

of dead pine wood and stumps per year, and annually clear more than 500,000 acres of cutover southern pine forests. Geographically the plants are located as follows:

Mississippi	—	6	Florida	-	1
Louisiana	—	4	Georgia	-	1
Alabama	—	2			

The supply of stumps has been estimated to last 15 to 30 years.

The products of this phase of the industry are known as steam-distilled (S.D.) wood naval stores, and include S.D. wood turpentine, S.D. dipentene, S.D. pine oil, and S.D. wood rosin.

As late as 1920 it was generally believed that within another ten years gum production would be at an end. This belief initiated the further development of the wood naval stores industry. About this time a method for recovering turpentine as a by-product from the alkaline sulfate pulping process of the paper industry was introduced. The crude turpentine is condensed from the vapors given off from the digesters during the cooking of pine wood. The crude sulfate turpentine is an amber colored, nauseating liquid containing 10 to 15 per cent sulfur-bearing compounds and even after refining will still impart a characteristic odor. Production has rapidly increased and today sulfate turpentine accounts for almost 30 per cent of the total United States production.

This process yields no rosin, but acidification of the digestion liquors yields a liquid, known as tall oil, which is a mixture of resin acids and fatty acids.

The processing plant of the Naval Stores Division of the Glidden Company at Jacksonville, Florida, has facilities for the refining of crude sulfate turpentine, in addition to the equipment for the destructive distillation of pine wood. This co-operative survey, however, was primarily concerned with

the liquid wastes resulting from the destructive distillation process.

The destructive distillation plant has been in continuous operation since about 1910.

7. Raw Materials

The principal raw material is the resinous wood of trunks and limbs of weathered pine trees, usually referred to as lightwood. About 85 species of pine in the United States are known to contain oleoresin, but because of their abundance only two -- longleaf yellow (Pinus palustris Miller) and slash (Pinus caribaea Morelet) -- are economically utilized. Longleaf pine is normally used at this plant and is preferred. The species of pine being used at the time of the study had not been definitely identified. It is not believed to be either longleaf or slash, although the chemical composition is similar to that of these species.

Stumps of the trees could be used, but because of the marshy terrain, near Fort Myers, Florida, where the wood is gathered, the trees have hardly any tap root.

The lightwood was left from previous lumbering operations, and from the original method of handling live trees in gum naval stores production, which frequently killed the tree or so weakened it that it fell during high winds common in the coastal states.

The wood structure is largely heartwood with comparatively thin sapwood. The heartwood is saturated with terpenes and resins making it almost impervious to attack by insects, fungi, or rot. The sapwood, or less durable portion, with small resin content, has largely been removed by decay. Lightwood that has been in or on the ground for five years or longer is preferred.

Green pine wood has an average moisture content of 50 per cent and weighs

about 52 pounds per cubic foot, while wood seasoned one year has an average moisture content of 20 per cent and weighs about 45 pounds per cubic foot. The seasoned wood (5 years or more) used at the Glidden Company plant has a moisture content of 8 to 12 per cent and weighs about 40 pounds per cubic foot.

The components of seasoned pine wood and the average percentage of each are as follows:

Lignin	--	30%
Hemicellulose	--	20%
Cellulose	--	50%

Chemically, the ultimate analysis of pine wood will range as follows:

Carbon	--	40 to 50%
Hydrogen	--	4 to 6%
Oxygen	--	35 to 45%
Ash	--	0.4 to 0.8%

In addition to the pine wood, other raw materials used include Bunker C fuel oil for heating the retorts and caustic soda for cleaning stills.

8. Composition and Uses of Derived Products

Destructively distilled wood products separate naturally according to their solubility and volatility into four groups; pyroligneous acid, wood tar, charcoal, and gas. Upon fractionation of the tar other commercially marketable products are obtained.

Pyroligneous acid is a dark red-brown liquid having a strong acid reaction and a peculiar empyreumatic odor. The yield of pyroligneous acid from softwood distillation is 50 to 60 per cent of the weight of the wood processed and has a specific gravity ranging from 1.020 to 1.030. The chemical composition is quite complex and includes many water soluble constituents. According to Klar (1) and Hawley (2) the following organic compounds have been identified in crude pyroligneous acid liquor from softwood distillation:

Water (80-90%)
* Formic acid
* Acetic acid
* Propionic acid
* Butyric acid
Valeric acid
Caproic acid
Crotonic acid
Angelic acid
Pyromucic acid
* Methyl alcohol
* Allyl alcohol
Acetaldehyde
Furfural
Methyl furfural
* Acetone
* Methyl ethyl ketone
* Ethyl propyl ketone
Dimethy acetal
Methylal
Valerolactone
* Methyl acetate
Pyrocatechol
* Ammonia
* Methylamine
Isoamyl alcohol
Formaldehyde
Pyroxonthen
Methyl formate
a-methyl b-keto-pentamethylene
Methyl propyl ketone
Pyridine
Isobutyl Alcohol
Keto-pentamethylene
Methyl pyridine

* occur in greatest quantities

Methyl alcohol, acetone, and acetic acid are economically distilled from hardwood pyroligneous acid, but in softwood distillation the yields are generally too small to give practicable recovery. One plant recovered acetate of lime and wood alcohol from softwood pyroligneous acid, but it was profitable only because of peculiar local conditions, which included a cheap supply of fuel for the refining process (2).

Crude pyroligneous acid has limited use as a disinfectant, weed killer, raw material for pyrolignite of iron, and as a meat curing and flavoring agent. These uses probably account for less than 2 per cent of the total production. The largest percentage goes to waste.

Tar is the term generally applied to those products resulting from the destructive distillation process which are not miscible with water. These products include both the light and heavy oils which are recovered from pyroligneous acid after gravity separation.

The chemical composition of wood tar is quite complex and extremely variable, but it is essentially a mixture of phenol acids and their derivatives together with some higher hydrocarbons of both the fatty and aromatic series.

Hawley (2) lists the following substances identified in tar and heavy oils:

Tar

Acetone
Sylvan
Toluene
Nitriles
m-xylene
Adipic ketone
Methyl acetate
Di-ethyl ketone
Valeric aldehyde
Di-methyl furan
Methyl propionate
Methyl n-butyrate
Methyl n-valerate
Tri-methyl furan
Methyl butyl ketone
Methyl ethyl ketone
Methyl propyl ketone
Unsaturated compounds
Polymerized compounds
Esters of unsaturated acids
Hydrochloric acid addition products

Heavy Oils (heavier than water with boiling points above 200°C.)

Phenol
Cresol
Phlorol
o-cresol
n-cresol
p-cresol
Guaiacol
Pyrogallol
Coerulignol
Pyrocatechin
1-3 xylenol-4
1-3 xylenol-5
Ethyl guaiacol
Pyrogallol di-methyl ether
Methyl pyrogallol di-methyl ether
Pyropyl pyrogallol di-methyl ether
Di-methyl ether of homopyrocatechin

The yield of crude tar oil averages about 50 gallons per ton of wood carbonized, and when further processed by steam distillation, to remove low boiling organic material, the resulting products are turpentine, dipentene, and pine oil. In addition the Glidden Company recovers two low-boiling solvents known commercially as "Laksol" and "Pinap." These five products account for 20 to 25 per cent of the total oil distillate. The residue, known as pine tar, is fairly well standardized and accounts for 75 to 80 per cent of the oil distillate.

Destructively distilled wood turpentine consists chiefly of terpene hydrocarbons, of which dipentene and p-cymene are major components. Terpinene and terpinolene are also present. Beta pinene is not usually present, and alpha pinene probably accounts for less than 10 per cent of the hydrocarbon portion. Small amounts of phenols, phenol ethers, furfural, and methyl

chavicol may also be present. This type of turpentine has a characteristic odor, and is a more powerful solvent than turpentine produced by other methods. It usually brings a lower price and finds greatest use as an industrial solvent. Turpentine is also used in paints, varnishes and lacquers. Other uses are in chemicals and pharmaceuticals, shoe polish and shoe materials, and in the synthesis of camphor.

Pine oil is distinctly a product of the heartwood and stumps of pine trees, and is not found in the exudations of living trees. Its composition depends upon the method of production, and consists principally of a mixture of tertiary and secondary terpene alcohols, together with smaller amounts of terpene oxides, ketones, and phenol ethers. Alpha-terpineol constitutes 50 to 60 per cent, other terpinols 15 to 25 per cent, and ketones and phenols 1 to 2 per cent. Pine oil also contains small amounts of vanillin, terpin hydrate and anethole.

Pine oil is used as a frothing agent in the mining industry for the separation of metal ores by the flotation process. It is also used as a wetting agent in the textile industry, and because of its germicidal properties is used as an ingredient of many liquid soaps, disinfectants, cattle sprays, preservatives, insecticides, deodorants, polishes, and sweeping oils.

Commercial dipentene is not a pure compound although dipentene is generally the major component. It is used as a softener in rubber processing and reclaiming, and as a pigment disperser and anti-skinning agent in paints.

"Laksol" and "Pinap" are low-boiling fractions of wood tar and find use as special solvents and anti-skinning agents.

Pine tar is used as a rubber compounding ingredient and to impregnate oakum and hemp ropes. It is also used in pharmaceuticals, soaps, salves, paints, shingle stains, tar paper, and paper bags for garment storage.

Charcoal is the residue left after dry distillation of wood at elevated

temperatures, and consists of carbon and inorganic constituents of the wood. High grade charcoal is porous, brittle, with conchoidal fracture, and retains the form of the wood. The yield is about 75 per cent of the volume and about 20 per cent of the weight of the wood. It burns with slight flame, without smoke and is easily ignited. Containing very little sulfur or phosphorus, it is especially useful in making certain grades of iron and steel. Other uses are in the compounding of explosives, chemical manufacture (carbon tetrachloride, carbon disulfide), household fuel, and in sugar and gasoline refining.

The non-condensable gases evolved during carbonization include the following:

Carbon dioxide	Ethane
Carbon monoxide	Ethylene
Methane	Hydrogen

These gases are returned to the power house for use as fuel for steam generation. No estimate is given as to the amount recovered.

9. Production

The average daily production based on 100 tons of wood processed was reported as follows:

"Lakeol"	100 gallons
"Pinap"	150 gallons
Turpentine	400 gallons
Dipentene	250 gallons
Pine oil	100 gallons
Total oils	1,000 gallons
Pine Tar	3,500 - 4,000 gallons
Charcoal	40,000 pounds
Pyroligneous Acid	15,000 gallons

The yield depends to a great extent on the resin content of the wood processed, which varies with the locality from which the wood was gathered, with the age of the wood, and with the age of the tree from which the wood

was derived.

10. Operations

The destructive distillation units of the Glidden Company plant at Jacksonville operate on a 24 hour cycle. Fluctuations in market demand for tar will influence production; however in recent years the plant has operated at capacity 7 days a week.

11. Employees

The destructive distillation plant employs approximately 75 persons exclusive of those engaged in wood gathering and hauling activities.

12. Water Supply

Water for plant processes is drawn from artesian wells. An estimated 1500 gallons per minute is used as cooling water in the destructive distillation plant. This water is not recirculated and is discharged directly to Moncrief Creek.

13. Waste Disposal

All process wastes from the destructive distillation plant, except condenser water, are discharged into settling ponds where some of the tar settles out. The wastes eventually reach Moncrief Creek by seepage through the earthen banks of the settling ponds. The settled tar is returned to the refinery for fractionation.

14. Sanitary Wastes

Sanitary wastes are discharged to the Jacksonville sewerage system. No evidence of sanitary wastes being discharged into the process waste sewers was found.

DESCRIPTION OF PROCESS

The Jacksonville Naval Stores Division of the Glidden Company has facilities for the refining of crude sulfate turpentine and for the destructive distillation of pine wood. This survey was primarily concerned with the liquid wastes resulting from the destructive distillation process and the discussion will be limited to this phase of the plant operations. The crude products obtained from this process are refined and modified in various ways to produce a variety of products collectively known as naval stores. The general operation of the plant is outlined below.

15. Wood Transportation and Storage

Seasoned pine wood from which most of the sapwood has been removed by weathering and natural deterioration, generally referred to as lightwood, is gathered in the field, cut into convenient lengths of about four feet, and shipped by rail to the plant. The wood used during this survey was obtained from marshy areas near Immokalee and Bonita Springs, Florida. After delivery to the plant the wood is stored in the yard until needed for process use. Storage space is available for stockpiling a 30 to 60 days supply for use when field activities are halted due to unfavorable weather.

16. Wood Distillation

Destructive distillation usually refers to the decomposition of organic matter by heat without access of air. Because the final residue of the decomposed substance consists chiefly of carbon the process is often referred to as carbonization.

The distillation or carbonization process is accomplished in oil fired retorts. The plant is equipped with eight retorts, of which six are normally in operation. The two retorts not in operation are held in stand-by status

or are undergoing maintenance. The retorts are constructed of heavy iron plate set in brickwork and consist of a distillation chamber, into which the wood is charged, completely surrounded by a combustion and heating chamber. Each retort is equipped with two condensers, consisting of coils of copper pipe surrounded by a water jacket or tank, for the recovery of the condensable products of the wood pyrolysis. The retorts are known as Michigan ovens and are standard within the industry.

Wood, with no preliminary treatment, is charged to the retorts by means of iron cars or buggies which run on steel rails. The buggies are about eight feet long, four feet wide, and are loaded to a height of about seven feet. The cars have removable slatted sides and ends for loading the wood and unloading the charcoal. The slatted sides allow the free access of heat and serve to retain the charcoal after carbonization.

Each buggy has a capacity of 2 1/2 tons of wood and each retort can accommodate 6 buggies. Thus, the total charge for each retort amounts to about 15 tons of wood.

One complete cycle of operation of a retort requires a period of about 24 hours. After the retort is charged with wood it is purged with steam to prevent the formation of explosive mixtures after distillation has begun. The retort, fired with Bunker "C" fuel oil, is heated as rapidly as practicable to a temperature of 800°F. It is estimated that this requires three to five hours. The retort operates at essentially atmospheric pressure.

Vapors and gases from the distillation pass through outlets in the retort and brickwork to the condensers which are of the vertical tubular type. The condensers have sufficient capacity to condense and cool the vapors during the peak load, although this may cover only a small portion of the distillation period.

The condensate is sent to settling tanks while the uncondensed gases are sent to the power house for use as fuel. The liquid obtained from the distillation consists of a ratio of approximately 1/4 oil and 3/4 water. During the first stage of the distillation cycle the liquid produced consists mainly of a mixture of water and light oil. After separation the oil will float on the water layer. The liquid product of the last portion of the cycle is a mixture of water and heavy oil. This oil after separation will settle below the water layer. For this reason the flow is split; the first portion of the distillate going to one collection tank, while the second portion goes to a second tank. There is no distinct break in the light and heavy oil production during the pyrolysis; considerable quantities of settled heavy oil are collected in the light oil collection tanks, and light oils accumulate above the water phase in the heavy oil collection tanks.

During the pyrolysis the temperature in the retort is maintained at 800° F. About 5 or 6 hours before the end of the cycle heating is discontinued and the retort slowly cooled. At the end of the cycle the buggies, now containing charcoal, are withdrawn from the retort and a fresh charge of wood admitted.

The hot charcoal from the retorts catches fire as soon as it comes in contact with the air and must, therefore, be cooled in closed ovens. These cooling ovens are made of heavy iron plate, without bottoms, and are about the same size as the retorts. The charcoal from the retorts is moved as rapidly as possible to the ovens and sand or earth is banked around bottom openings to prevent the access of air. The charcoal remains in the cooling ovens about 24 hours.

During the pyrolysis, which is an exothermic reaction, the oleoresin in the wood is cracked to form pine tar oils. Some oils are also derived from

the lignins and cellulose of the wood. At the higher temperatures rosin loses carbon dioxide to form neutral oils. The pyrolysis of 100 tons of wood in this plant normally produces 4,500 to 5,000 gallons of oil, about 15,000 gallons of pyroligneous acid liquor, and about 20 tons of charcoal. The amount of non-condensed gases is not estimated.

17. Separation and Distillation

The crude distillate from the retorts is stored in wooden collection tanks where the mixture separates into a pyroligneous acid layer and crude pine tar oil layers. Heavy oils will settle below the aqueous phase and the light oils will float on the surface. Mutual solubilities as well as varying degrees of emulsification prevent complete separation. The separated oil from the collection tanks, known as "drawn oil," is introduced into a steam heated still, heated to about 100°C., and allowed to settle for approximately one hour. Additional water is separated by this procedure and is sent to pyroligneous acid liquor waste tanks. Distillation is started following this separation. The distillate is condensed and separated. Relatively clean condenser cooling water is discharged to Moncrief Creek and the separated water is decanted to a settling pond.

The organic phase of the distillate, known as first run light oils, which accounts for 20 to 25 per cent of the weight of the drawn oil, is fractionated into the following five solvents:

Solvent	Distilling Range
"Laksol"	90 - 125°C.
"Pinap"	120 - 150°C.
D.D. Turpentine	150 - 180°C.
D.D. Dipentene	175 - 195°C.
D.D. Pine Oil	190 - 225°C.

The residual from the still is pine tar and accounts for 75 to 80 percent of the weight of

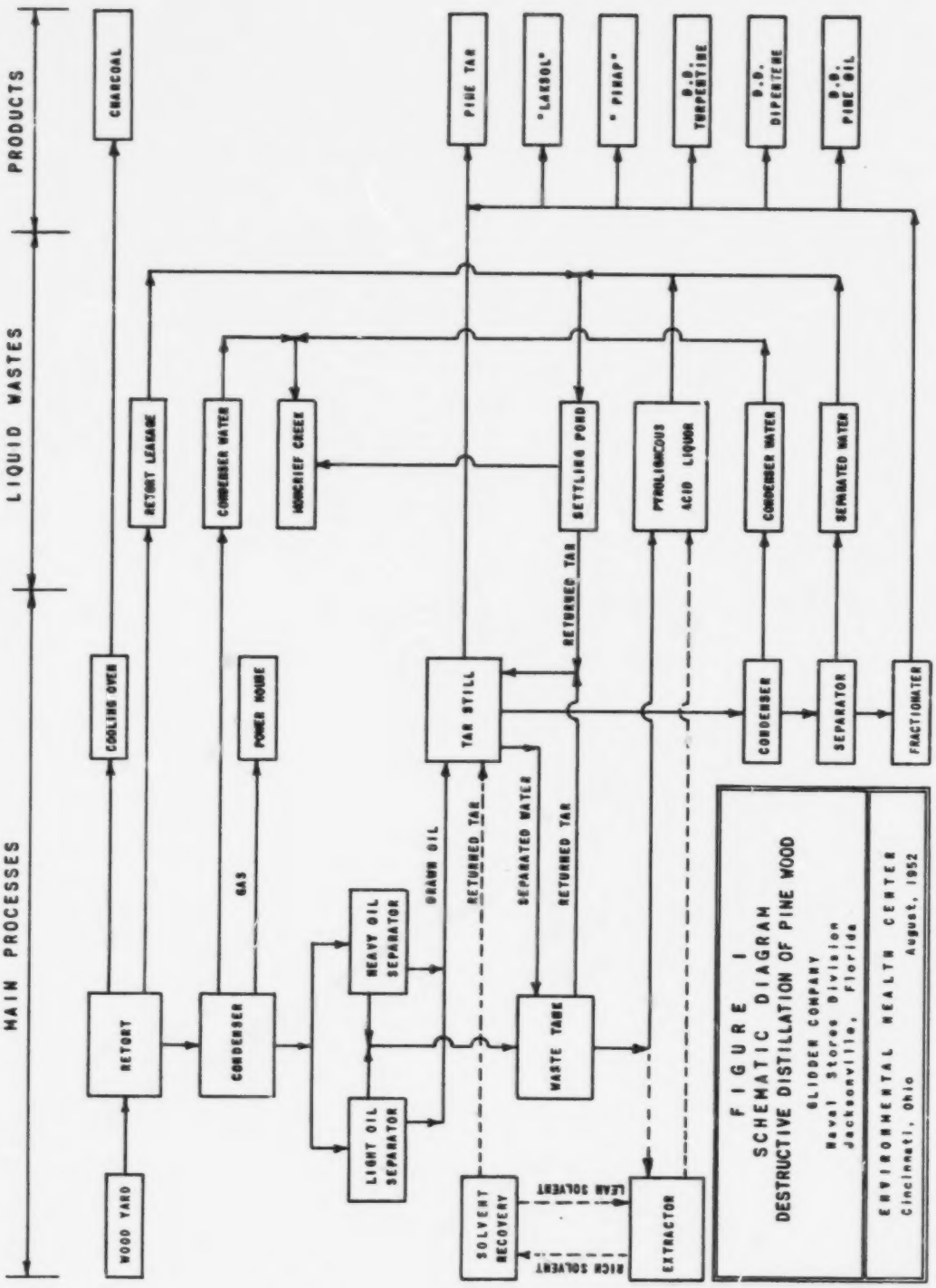
the drawn oil. The pine tar is shipped without further refining.

The water phase, known as pyroligneous acid liquor, from the separation tanks, is pumped to two waste tanks in series. The waste has a theoretical detention of four days, each tank having a capacity of 30,000 gallons. About 30 per cent of the total tar oils from the destructive distillation process are still emulsified in this liquor. Further separation takes place in these tanks; an average of 1,000 gallons of oil are recovered per day and sent to the tar still. The overflow from the final waste tank flows to settling ponds where an additional 500 to 1,000 gallons of oil are recovered per day. Two settling ponds are currently being used and provide a combined retention of about two days. In addition to the pyroligneous acid liquor, some tar and water from retort leakage is picked up by sump pumps and discharged to the ponds. There is no direct outlet from either of the two ponds. The waste, however, eventually reaches Moncrief Creek by seepage through earthen banks.

18. Extraction of Pyroligneous Acid Liquor

Preliminary activities in the operation of an extraction unit to process the waste pyroligneous acid liquor were in progress at the time of this investigation. It is anticipated that the pyroligneous acid liquor will be extracted with light solvent fractions from the destructive distillation process to recover tars and oils. Based on a few days operations it was found that from 100 to 1500 gallons of tar per day could be extracted and recovered by this method. This amount was not entirely a net gain however, as some of the tar would have settled out in the ponds and subsequently been recovered.

A schematic diagram of the destructive distillation of pine wood showing main processes, liquid wastes, and marketable products is presented in Figure 1. The proposed extraction process is designated by broken lines.


MAIN PROCESSES
LIQUID WASTES
PRODUCTS
WOOD YARD
RETORT
CONDENSER
COOLING OVEN
POWER HOUSE
LIGHT OIL SEPARATOR
HEAVY OIL SEPARATOR
SOLVENT RECOVERY
EXTRACTOR
WASTE TANK
TAR STILL
CONDENSER
SEPARATOR
FRACTIONATER
CHARCOAL
RETORT LEAKAGE
CONDENSER WATER
HORSERIEF CREEK
SETTLING POND
PYROLIGNEOUS ACID LIQUOR
CONDENSER WATER
SEPARATED WATER
PINE TAR
"LAROL"
" PINAP"
D.O. TURPENTINE
D.O. DIPENTENE
D.O. PINE OIL
GAS
DRAWN OIL
RETURNED TAR
SEPARATED WATER
RETURNED TAR
RETURNED TAR
LEAN SOLVENT
RICH SOLVENT
FIGURE I
SCHEMATIC DIAGRAM
DESTRUCTIVE DISTILLATION OF PINE WOOD
GLIDDEN COMPANY
Naval Stores Division
Jacksonville, Florida
ENVIRONMENTAL HEALTH CENTER
Cincinnati, Ohio
August, 1952

SURVEY PROCEDURES

19. Sample Collection

During the survey, samples were collected jointly by personnel of the U. S. Public Health Service and the Glidden Company from the following sources:

(1) Pyroligneous acid liquor from final waste tank
(2) Extracted pyroligneous acid liquor
(3) Pyroligneous acid liquor from first settling pond
(4) Retort condenser cooling water

Samples were not composited as the large volume of the waste tank and pond, from which the samples were collected, assured a representative mixture. Care was taken in the collection of the individual daily samples so that floating oils and oil "pockets," which are normally recovered, were not included in the sample. The extracted pyroligneous acid liquor sample was obtained by dividing the sample from the pyroligneous acid liquor waste tank into two portions; one portion retaining its original composition and the other portion having some of the tars and oils removed by laboratory extraction. In this way the efficiency of the solvent extraction could be directly determined.

Retort condenser cooling water samples were collected daily from the effluent pipe just before the waste entered Moncrief Creek.

20. Flow Measurements

The quantity of liquid waste being discharged by the various plant units was determined by Glidden Company personnel. These determinations were made by accurately timing the liquid level rise in calibrated tanks. The following figures were used in calculating daily quantities of significant constituents being discharged:

Waste	Discharge Gallons Per Day
(1) Pyroligneous acid liquor from final waste tank	15,000
(2) Extracted pyroligneous acid liquor	15,000
(3) Pyroligneous acid liquor from first settling pond	15,000
(4) Retort condenser cooling water	2,220,000

21. Laboratory Analyses

All or part of the following laboratory determinations were made on the samples collected:

Immediate Oxygen Demand
Biochemical Oxygen Demand
Oxygen Consumed
Volatile Acids
Acidity
Alkalinity
pH
Color
Phenols
Ether Extractable Material
Lignin and Tannin
Sulfides
Total Solids, Total, Volatile, and Fixed
Suspended Solids, Total, Volatile, and Fixed

The procedures followed in making the above analyses are, in general, as given in "Standard Methods for the Examination of Water and Sewage," 9th Edition (3). Modifications of the procedures used for the determination of phenols, ether extractable material, and oxygen consumed are given in the appendix of this report.

EXPLANATION OF LABORATORY ANALYSES

22. Immediate Oxygen Demand

Certain compounds when present in liquid wastes combine with available oxygen in a relatively short period of time. The amount of oxygen utilized by a waste within 15 minutes of mixing with dillution water of known oxygen con-

tent is known as immediate oxygen demand. This analysis is of special value as an aid in determining the amount of oxygen that must be provided by receiving streams during the course of stabilization.

23. Biochemical Oxygen Demand (B.O.D.)

The biochemical oxygen demand of sewage, sewage effluents, polluted waters, or industrial wastes, is the oxygen required during stabilization of the decomposable organic matter by aerobic bacterial action. Since this is a phenomenon into which both time and temperature enter, a standard set of conditions (5 days at 20° C.) is universally used for the test. For normal domestic sewage and some industrial wastes, approximately 68 per cent of the oxygen requirement of the carbonaceous material present is satisfied during the standard test. Because of the variable carbon-nitrogen ratio of industrial wastes, however, the rate of oxygen demand of such wastes may not follow the typical oxidation curve for domestic sewage. Results are expressed in parts per million (p.p.m.).

24. Oxygen Consumed

The oxygen consumed test is a measure of the chemical oxidant required to oxidize the organic matter present in a sample under particular standard conditions. The test is of value in estimating the strength of certain industrial wastes, and in conjunction with the B.O.D. determination. It can be used where it would be to an advantage to obtain results indicative of oxygen demand in less time than the biochemical oxygen demand test requires. Results are expressed in parts per million oxygen.

25. Volatile Acids

The procedure for determining volatile acids in an industrial waste is quite empirical and is not intended for accurate analyses. It does, however, give limited information concerning the quantity of volatile compounds

in the waste. The results are expressed as parts per million volatile acids as acetic acid. Other acids present in the waste that can be classified as volatile include formic, butyric, and propionic.

26. Acidity

Acidity of a water or waste is usually caused by the presence of uncombined carbon dioxide, mineral acids and salts of strong acids and weak bases. By using phenolphthalein and methyl orange indicators the amount of each type of acidity present can be determined. Phenolphthalein acidity is usually referred to as total acidity, while methyl orange acidity is referred to as mineral acidity. Results are expressed as parts per million calcium carbonate ($CaCO_3$).

27. Alkalinity

Alkalinity of a water or waste represents the carbonates, bicarbonates, hydroides, and occasionally the borates, silicates, and phosphates of the alkali and alkali earth metals. By use of the phenolphthalein and methyl orange end points, the amount of each type of alkalinity can be determined. Methyl orange alkalinity is usually referred to as total alkalinity. Calcium and magnesium account for most of the alkalinity present in a sample. Results are expressed as parts per million calcium carbonate ($CaCO_3$).

28. pH

The symbol pH denotes the negative logarithm (to the base 10) of the hydrogen ion concentration of a solution, this symbol being a universal one in chemistry. The pH value indicates the relative acidity or alkalinity of a water or waste, being lower with higher degrees of acidity. It is a measure of intensity rather than quantity. All pH determinations, during this survey, were made using a Beckman electrometric pH meter, Model G.

29. Color

True color of a water or waste is due to the presence of coloring matter in solution. Apparent color is due to color in suspension in the liquid and can be removed by sedimentation or filtration. True color is usually caused by extracts of decomposing vegetable matter or, in the case of industrial wastes, by chemicals or compounds from processing various raw materials. Color is expressed in parts per million and is measured by comparing the water sample with prepared standards of potassium chloroplatinate. Apparent color determinations were not made on any samples during this survey.

30. Phenols

The laboratory determinations for phenols indicate the gross phenol content including cresols and higher phenols. These substances are found in variable proportions and amounts in certain industrial wastes.

Phenols in quantities as low as 0.002 to 0.005 parts per million in the presence of chlorine will produce chlorophenol (medicinal) tastes and odors in water. A concentration of 0.1 part per million of phenol alone imparts to water the characteristic taste and odor of phenol. In fish, phenol produces paralysis of the neuromuscular mechanism and hemolyzes the blood.

31. Ether Extractable Material

Ether extractable materials include such substances as oils, greases and tars. The presence of these pollutants renders water difficult and sometimes impractical to treat, either for industrial or domestic use. In addition, these substances make beaches unsightly, coat watercraft, and are hazards to fish and waterfowl. Results of laboratory determinations are expressed in parts per million.

32. Tannin and Lignin

The exact chemical composition of tannin and lignin is not known. These compounds are more or less soluble in water and exhibit characteristic colors in aqueous solutions. Lignins in combination with phenols and organic bases give colors ranging from yellow to dark red. Tannin extracts from wood, in aqueous solutions, range in color from light straw to dark red or brown. In addition all tannins are polyhydroxylic phenols and exhibit a marked tendency to absorb oxygen (4). The lignin and tannin determination serves as an aid in evaluating the nature of waters or wastes. Results are expressed in parts per million tannin and lignin as tannic acid.

33. Sulfides

The sulfide determination is a measure of the total sulfide content of a water or waste, and includes dissolved sulfides and acid soluble metallic sulfides present as suspended matter. Sulfides have an objectionable odor, are toxic to fish in low concentrations, and are easily oxidized which creates an immediate oxygen demand in the receiving stream.

34. Solids

The determination of solids includes those for total and suspended solids as well as their volatile constituents. Total solids consist of all the solids present in a liquid. The term includes both suspended and dissolved solids. Suspended solids are in suspension or float on the surface of water, sewage or other liquid, and are removed by laboratory filtration. Dissolved solids are found by subtracting suspended solids from total solids. Volatile solids are those that are lost upon ignition of total solids (giving total volatile solids) or suspended solids (giving suspended volatile solids). Fixed solids are determined by subtracting total volatile solids from total solids (giving total

fixed solids) or suspended volatile solids from total suspended solids (giving fixed suspended solids). Volatile solids represent approximately the amount of organic matter, and fixed solids the inorganic matter in a water or liquid waste.

Suspended solids in streams cause water to be turbid and unsightly and may be deposited in streams, interfering with navigation, and injury to the habitat of fish.

35. Population Equivalent

Normal domestic sewages, relatively free from industrial wastes, possess characteristics which are reasonably well defined, and it is, therefore, possible to compare them on a common basis. Industrial wastes are influenced by the processes from which they originate and the characteristics are not readily defined by the same standards. The "Population Equivalent" value, therefore, provides a basis on which industrial wastes may be compared to domestic sewages. The coefficient,

0.17 pounds of 5-day, 20°C., B.O.D. per capita per day,

used in comparing domestic sewages, has been used in converting the data to a population equivalent basis.

DISCUSSION OF RESULTS

The destructive distillation unit of the Glidden Company plant operates continuously and because of nearly uniform daily operations the strengths of the wastes can be rather closely correlated with production.

A minimum of ten samples were collected from each source and the average results were used as representative values of the different constituents of the wastes. Some variations were noted in results of individual daily

samples. These were due, in part, to indeterminate storage periods throughout the process and to the character of the wastes that made the collection of representative samples rather uncertain. In most cases the variations in daily samples were within reasonable limits; one exception was the retort condenser cooling water which varied considerably.

Tables 1 and 2 show the important findings of the survey. Table 1 presents the average concentration of significant constituents of the wastes sampled, while table 2 presents the average daily quantities of these constituents.

Table 1 - Average Concentration of Significant Constituents

Constituent	Source	Pyroligneous Acid Liquor from Final Waste Tank	Extracted Pyroligneous Acid Liquor	Pyroligneous Acid Liquor From First Settling Pond	Retort Condenser Cooling Water
Discharge	M.G.D.	0.015	0.015	0.015	2.22
Immediate Oxygen Demand	p.p.m.	3,620	4,280	1,160	-
B.O.D., 5 Day-20°C.	p.p.m.	66,100	66,800	31,800	26
Oxygen Consumed	p.p.m.	140,000	124,000	50,100	-
Volatile Acids as Acetic Acid	p.p.m.	23,900	24,900	13,800	-
Acidity	p.p.m.	23,600 P 17,600 M	23,100 P 17,600 M	12,800 P 9,350 M	
Alkalinity	p.p.m.				152 M
pH	range	2.3-4.1	2.4-4.1	2.8-3.2	7.1-8.4
Color	p.p.m.	4,000	4,700	3,700	42
Phenols	p.p.m.	1,980	1,180	634	< 0.01
Ether Extractable Material	p.p.m.	22,200	7,270	3,420	-
Sulfides as S	p.p.m.	-	-	-	< 0.1
Lignin and Tannin as Tannic Acid	p.p.m.	71,200	68,500	30,600	-
Total Solids,	Total p.p.m.	39,500	33,600	19,300	-
	Volatile p.p.m.	37,700	32,300	17,900	-
	Fixed p.p.m.	1,800	1,300	1,400	-
Suspended Solids,	Total p.p.m.	1,250	31	23	-
	Volatile p.p.m.	1,210	31	23	-
	Fixed p.p.m.	40	0	0	-
Dissolved Solids,	Total p.p.m.	38,200	33,600	19,300	-

P - Phenolphthalein
M - Methyl Orange

Table 2 - Average Daily Quantities of Significant Constituents

Constituent		Source	Pyroligneous Acid Liquor From Final Waste Tank	Extracted Pyroligneous Acid Liquor	Pyroligneous Acid Liquor from First Settling Pond	Retort Condenser Cooling Water
Discharge		M.G.D.	0.015	0.015	0.015	2.22
Immediate Oxygen Demand		Lbs/Day	453	535	185	-
B.O.D., 5 Day-20°C.		Lbs/Day	8,270	8,360	3,920	472
Oxygen Consumed		Lbs/Day	17,500	15,500	7,390	-
Volatile Acids as Acetic Acid		Lbs/Day	2,990	3,120	1,730	-
Color		Lbs/Day	495	590	463	777
Phenols		Lbs/Day	247	138	104	< 0.2
Ether Extractable Material		Lbs/Day	2,780	910	428	-
Sulfides as S		Lbs/Day	-	-	-	< 2
Lignin and Tannin as Tannic Acid		Lbs/Day	8,910	8,580	3,820	-
Total Solids,	Total	Lbs/Day	4,940	4,200	2,410	-
	Volatile	Lbs/Day	4,720	4,040	2,240	-
	Fixed	Lbs/Day	220	160	170	-
Suspended Solids,	Total	Lbs/Day	156	4	3	-
	Volatile	Lbs/Day	151	4	3	-
	Fixed	Lbs/Day	5	0	0	-
Dissolved Solids,	Total	Lbs/Day	4,780	4,200	2,410	-

The average daily liquid waste discharge from the destructive distillation unit amounted to 2.24 million gallons. Retort condenser cooling water contributed 2.22 m.g.d., and pyroligneous acid liquor 0.015 m.g.d. Discharge figures furnished by the Glidden Company were used in computing daily quantities of constituents. Even though daily variations in discharge did occur these figures were considered to remain constant during the survey. Pyroligneous acid liquor was sampled at three points in the plant, but was in effect the same waste with different degrees of treatment.

Retort condenser cooling water is pumped directly to the condensers from artesian wells, and discharged without further use or treatment. Six of the ten samples collected from this source presented little or no evidence of contamination, while four samples showed definite degrees of contamination. These four samples showed increases in B.O.D. and color concentration with a corresponding decrease in pH. This contamination was undoubtedly caused by condenser leakage. One important fact to be noted from the results of sampling this waste is the wide variations in B.O.D. values, which ranged in magnitude from 4 to 1,740 pounds of 5 day B.O.D. discharged daily.

Pyroligneous acid liquor is an extremely complex mixture containing at least 35 identifiable compounds. The samples designated as "Pyroligneous acid liquor from final waste tank" consisted of the raw waste from the wood pyrolysis and is normally pumped to the settling ponds in this form. The raw waste is inhibitory to biological action; partly because of the low pH, which ranged from 2.3 to 4.1, but mainly because of the numerous organic compounds present which have bactericidal properties. B.O.D. values, obtained from 1:1,000 dilutions, averaged 66,100 p.p.m. This concentration resulted in an average daily discharge of 8,270 pounds of 5 day B.O.D. Concentrations of other constituents

were also comparatively high. Of special importance are the high concentrations of color, phenol, ether extractable material, and lignin and tannin. Ether extractable material represents the oil content of the waste which could be refined and marketed if economical means of recovery were devised. The quantity of this material discharged daily averaged 2,780 pounds.

Color, phenols, and lignins and tannins are all interrelated in that tannins are polyhydoxylic phenols. Lignins in combination with phenols, in aqueous solutions, will give colors ranging from yellow to dark red. These compounds, in wastes that are discharged to receiving streams, are therefore objectionable for at least two reasons; the toxic qualities that inhibit aquatic life, and the color which is undesirable for aesthetic reasons.

Samples designated "Extracted pyroligneous acid liquor" were raw waste samples with some of the tar and oil removed by solvent extraction. All analyses were made on laboratory extracted samples, and the results are only indicative of what might occur on a full scale plant application. Extraction on a continuous basis was to be initiated by the company at the close of the survey. Changes in average daily quantities of significant constituents due to solvent extraction are presented in table 3. Ether extractable material decreased 67.2 per cent while the B.O.D. showed an increase of 1.0 per cent. This indicates that the majority of the B.O.D. producing substances were not contained in the oil and tar, but rather in the aqueous phase of the waste. Color concentration increased 19.1 per cent. This phenomenon has not been adequately explained. Grantham (5) found that neutralization of pyroligneous acid from softwood distillation also increased the color. The pH values of the extracted waste samples remained in the same range as those of the raw waste. Lignins and tannins, which are insoluble in the extraction solvent,

showed only a slight decrease in concentration.

Samples designated as "Pyroligneous acid liquor from first settling pond" were surface samples collected from the first lagoon. This waste was raw (not extracted) pyroligneous acid liquor after approximately two days detention. The decreases in average daily quantities of significant constituents due to lagooning are presented in table 4. Ether extractable material was decreased 84.6 per cent. This amounted to 2,350 pounds per day of which the majority was recovered and sent back to the plant for refining. B.O.D. reduction, which

Table 3 - Per Centage Changes in Average Daily Quantities of Significant Constituents Due to Solvent Extraction

Source / Constituent	Pyroligneous Acid Liquor From Final Waste Tank Lbs/Day	Extracted Pyroligneous Acid Liquor Lbs/Day	Difference Lbs/Day	Increase Per Cent	Decrease Per Cent
Immediate Oxygen Demand	453	535	+ 82	18.1	
B.O.D., 5 Day-20°C.	8,270	8,360	+ 90	1.0	
Oxygen Consumed	17,500	15,500	- 2,000		11.4
Volatile Acids as Acetic Acid	2,990	3,120	+ 130	4.3	
Color	495	590	+ 95	19.1	
Phenols	247	138	- 109		44.1
Ether Extractable Material	2,780	910	- 1,870		67.2
Lignin and Tannin as Tannic Acid	8,910	8,580	- 330		3.7
Total Solids, Total	4,940	4,200	- 740		15.0
Volatile	4,720	4,040	- 680		14.4
Fixed	220	160	- 60		27.3
Suspended Solids, Total	156	4	- 152		97.4
Volatile	151	4	- 147		97.4
Fixed	5	0	- 5		100.0
Dissolved Solids, Total	4,780	4,200	- 580		12.1

Table 4 - Decrease in Average Daily Quantities of Significant Constituents Due to Lagooning

Source / Constituent	Pyroligneous Acid Liquor From Final Waste Tank Lbs/Day	Pyroligneous Acid Liquor From First Settling Pond Lbs/Day	Decrease Lbs/Day	Decrease Per Cent
Immediate Oxygen Demand	453	145	308	68.0
B.O.D., 5 Day-20°C.	8,270	3,920	4,350	52.6
Oxygen Consumed	17,500	7,390	10,110	57.8
Volatile Acids as Acetic Acid	2,990	1,730	1,260	42.1
Color	495	463	32	6.5
Phenols	247	104	143	57.9
Ether Extractable Material	2,780	428	2,350	84.6
Lignin and Tannin as Tannic Acid	8,910	3,820	5,090	57.1
Total Solids, Total	4,960	2,410	2,550	51.3
Volatile	4,720	2,240	2,480	52.5
Fixed	220	170	50	22.7
Suspended Solids, Total	156	3	153	98.1
Volatile	151	3	148	98.0
Fixed	5	0	5	100.0
Dissolved Solids, Total	4,780	2,410	2,370	49.5

amounted to 52.6 per cent was not due to biological decomposition, but to chemical oxidation of organic constituents. Lignins and tannins in particular are readily oxidized. Color reduction, which was the least of any of the constituents, amounted to 6.5 per cent.

The settling pond has no direct outlet to Moncrief Creek but from physical inspection it is an obvious fact that the wastes do enter the stream by seepage through the earthen banks. Analyses of the waste as it entered the stream were not made during this survey, and the difference in composition between the pond effluent and the pond surface samples is not definitely known. Schmidt (6) found that the B.O.D. decreased from 26,900 p.p.m., as it was initially discharged, to 18,886 p.p.m. as it enters the stream after seeping through the dike.

Daily data summary sheets for all sample points are included in the appendix of this report.

SUMMARY

Based on data and supporting information presented in this report certain points may be summarized as follows:

36. Quantity of Liquid Wastes Discharged

The average daily discharge amounted to 2.235 million gallons, distributed as follows:

Source	Discharge
Retort Condenser Cooling Water	2.22 m.g.d.
Pyroligneous Acid Liquor	0.015 m.g.d.

37. Population Equivalent

Population equivalents of the various wastes, based on 0.17 pounds 5 day B.O.D. per capita per day, are as follows:

Source	Population Equivalent
Retort Condenser Cooling Water	2,780
Pyroligneous Acid Liquor from Final Waste Tank	48,650
Extracted Pyroligneous Acid Liquor	49,200
Pyroligneous Acid Liquor from First Settling Pond	23,000

38. Unit Values

The unit values for wastes and constituents resulting from the processing of one ton of wood are as follows:

		Pyroligneous Acid Liquor			Retort Condenser
		Raw	Extracted	Settled	Cooling Water
Liquid Waste,	gallons	150.	150	150.	22,200
5 Day B.O.D.,	pounds	82.7	83.6	39.2	4.7
Immediate Oxygen Demand,	pounds	4.5	5.4	1.4	-
Oxygen Consumed,	pounds	175.	155.	74.	-
Ether Extractable Material,	pounds	27.8	9.1	4.3	-
Volatile Acids,	pounds	29.9	31.2	17.3	-
Phenols,	pounds	2.5	1.4	1.0	-
Lignin and Tannin,	pounds	89.1	85.8	38.2	-
Total Solids,	pounds	49.4	42.0	24.1	-
Suspended Solids,	pounds	1.6	0.04	0.03	-
Dissolved Solids,	pounds	47.8	42.0	24.1	-
Population Equivalent,	persons	486.	492.	230.	27.8

39. **Average Yield**

The average yields of charcoal and liquid products per ton of seasoned pine wood processed are as follows:

Product	Yield
"Laksol"	1.0 gallon
"Pinap"	1.5 gallons
Turpentine	4.0 gallons
Dipentene	2.5 gallons
Pine Oil	1.0 gallon
Pine Tar	35-40 gallons
Charcoal	400 pounds
Pyroligneous Acid Liquor	150 gallons

A C K N O W L E D G M E N T

It is desired to express appreciation to Dr. J. P. Bain, Technical and Research Director of the Jacksonville Naval Stores Division of the Glidden Company, for his co-operation and counsel extended during this survey. Special mention must be made of Mr. A. B. Booth, Research Chemist, who gave generously of his time in supplying special laboratory samples.

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BIBLIOGRAPHY

(1) Klar, M. The Technology of Wood Distillation. Trans. Alex. Rule. New York: D. Van Nostrand Co., 1925.

(2) Hawley, L. F. Wood Distillation. A.C.S. Monograph Series No. 13. The Chemical Catalog Co., 1923.

(3) American Public Health Association. Standard Methods for the Examination of Water and Sewage. 9th ed. New York, 1946.

(4) Kurth, E. F. Wood Chemistry. Ed. L. E. Wise. Chapter 12, "The Extraneous Components of Wood." A.C.S. Monograph Series. New York: Reinhold Publishing Co., 1946.

(5) Grantham, G. R. Industrial Waste Study. Final Report on Project No.4907. Eng. and Ind. Exp. Sta., University of Florida, Gainesville, 1951.

(6) Schmidt, J. D. Moncrief Creek Pollution Survey. Duval County. Fla. State Board of Health, Bur. San. Eng. Jacksonville, 1951.

(7) Statistical Abstract of the United States. U. S. Dept. Comm., Bur. of the Census. Washington, 1952. Sections on "Manufacturing in the United States."

(8) McBride, R. S. Marketing and Industrial Uses of Charcoal. Chem. & Met. Eng., 39. 664 (1932).

(9) Crops in Peace and War. Yearbook of Agriculture, 1950-1951. U. S. Dept.Agr. Washington, 1951. Articles on "Crops from the Forests."

(10) Palmer, R. C. Producing Naval Stores From Waste Pine Wood. Chem. and Met. Eng., 37. 289 (1930).

(11) McBride, R. S. Hardwood Distillation Faces New Economic and Raw Material Problems. Chem. and Met. Eng., 39, 534 (1932).

(12) McBride, R. S. Chemical Engineering Problems in Hardwood Distillation. Chem. and Met. Eng., 39, 604 (1932).

(13) Walker, George. Methods for the Utilization of Wood Waste. J. Soc. Chem. Ind., 30, 934 (1911).

(14) Illick, J. S. An Outline of General Forestry. New York: Barnes and Noble. 1939.

(15) Humphrey, I. W. Extraction of Terpene Chemicals from Waste Pine Wood. Trans. Inst. Chem. Engrs. (London). 9, 40 (1931).

(16) Van Romaine, Eldon. Naval Stores 1919-1939. Part 1, Chem. Ind., 45, 259 (1939). Part 2. Chem. Ind., 45, 402 (1939).

(17) Pritchard, T. W. Some Recent Developments in Wood Distillation. Ind. Eng. Chem., 4, 338 (1912).

(18) Garvie, W. The Wood Naval Stores Industry : Its Rise and Development. Chem. Age (London). 39, 387 (1938).

(19) Naval Stores - History, Production, Distribution and Consumption. Ed. Thomas Gamble. Savannah, Ga.: Review Publishing and Printing Co., 1921.

(20) Goldblatt, Leo. The Essential Oils. Ed. Ernest Guenther, vol.VI. Chap. XX "Essential Oils of the Family Pinaceae; American Turpentines." New York; D. Van Nostrand Co., 1952.

(21) Peterson, J. M. History of the Naval Stores Industry in America. Part 1, J. Chem. Educ., 16, 203 (May 1939). Part 2, J. Chem. Educ., 16, 317. (July 1939).

(22) Teeple, J. E. Pine Products from Pine Woods. Ind. Eng. Chem., 1, 597 (1909).

(23) Paul, A. E. Turpentine and its Adulterants. Ind. Eng. Chem., 1, 27 (1909).

(24) Frankforter, G. B. Waste Wood and its Utilization. Ind. Eng. Chem., 3, 4 (1911).

(25) Wood Distillation. Trade Notes. Ind. Eng. Chem., 3, 57 (1911).

(26) Schantz, J. L. and Marvin, Theodore. Waste Utilization. Ind. Eng. Chem. 31, 585 (1939).

(27) Healy, J. B. Distilling Pine Products at New Orleans. Chem. and Met. Eng., 43, 20 (1936).

(28) Othmer, D. F. and Katzen, Raphael. Tar Elimination in Pyroligneous Acid. Ind. Eng. Chem., 35, 289 (1943).

(29) Wood Naval Stores Waste Studies. Environmental Health Center, U.S.Public Health Service, Cincinnati, Ohio, 1950. (Unpublished Reports).

APPENDIX

GLIDDEN COMPANY
NAVAL STORES DIVISION
JACKSONVILLE, FLORIDA

U. S. PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

Source - Pyroligneous Acid Liquor from First Settling Pond

Data Summary Sheet

Date 1952	Immediate Oxygen Demand	B.O.D. 5 Day-20°C.	Color	pH	Acidity	Lignin and Tannin as Tannic Acid	Volatile Acids as Acetic Acid	Phenols	Ether Extractable Material	Oxygen Consumed	Solids					
											Total			Suspended		
											Total	Volatile	Fixed	Total	Volatile	Fixed
2/13	1,200	43,200	5,000	2.8	17,000 P 13,100 M	-	18,700	984	3,360	83,100	21,900	20,200	1,700	14	14	0
2/14	200	51,400	4,000	2.8	16,900 P 13,200 M	55,000	20,400	1,080	3,230	78,800	21,300	20,200	1,100	26	26	0
2/18	600	26,400	3,000	3.1	10,900 P 8,400 M	25,000	12,200	715	3,780	54,300	14,700	13,300	1,400	30	30	0
2/19	1,200	20,600	3,500	3.1	8,740 P 6,720 M	22,500	10,400	597	3,660	42,500						
2/20	200	26,200	4,000	3.2	10,900 P 8,220 M	26,200	12,700	743	2,960	58,700						
2/21	1,400	24,200	3,500	3.1	12,100 P 8,460 M	27,500	12,900	-	3,120	49,400						
2/25	700	30,400	4,000	3.0	12,000 P 8,720 M	30,000	13,100	787	3,200	49,700						
2/26	1,500	28,200	3,000	3.1	10,300 P 8,060 M	26,200	11,700	736	3,100	55,600						
2/27	2,000	32,400	3,500	3.0	11,700 P 8,740 M	30,000	12,000	871	3,620	57,100						
2/28	2,600	34,500	3,500	3.0	13,000 P 9,840 M	32,500	14,200	994	4,170	61,500						
Mean	1,160	31,800	3,970		12,400 P 9,350 M	30,600	13,800	834	3,420	50,100	19,300	17,900	1,400	23	23	0
Max.	2,600	51,400	5,000	3.2	17,000 P 13,200 M	55,000	20,400	1,080	4,170	83,100	21,900	20,200	1,700	30	30	0
Min.	200	20,600	3,000	2.8	8,740 P 6,720 M	22,500	10,400	597	2,960	42,500	14,700	13,300	1,100	14	14	0

P - Phenolphthalein
M - Methyl Orange

All results expressed in parts per million

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CO-OPERATIVE INDUSTRIAL WASTE SURVEY

GLIDDEN COMPANY
NAVAL STORES DIVISION
JACKSONVILLE, FLORIDA

U. S. PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

Source - Pyroligneous Acid Liquor from First Settling Pond — Data Summary Sheet

Date 1952	Immediate Oxygen Demand	B.O.D. 5 Day - 20°C.	Color	Lignin and Tannin — as Tannic Acid	Volatile Acids as Acetic Acid	Phenols	Ether Extractable Material	Oxygen Consumed	Solids					
									Total			Suspended		
									Total	Volatile	Fixed	Total	Volatile	Fixed
2/13	150	5,400	625	-	2,340	123	420	10,400	2,740	2,530	210	2	2	0
2/14	25	6,430	500	6,880	2,550	135	484	9,860	2,660	2,530	130	3	3	0
2/18	75	3,300	375	3,130	1,530	89	473	6,790	1,840	1,660	180	4	4	0
2/19	150	2,580	438	2,810	1,300	75	458	5,320						
2/20	25	3,230	500	3,280	1,590	93	370	7,340						
2/21	175	3,030	438	3,440	1,610	-	390	6,180						
2/25	88	3,800	500	3,750	1,640	98	460	6,220						
2/26	188	3,530	375	3,280	1,460	92	388	6,960						
2/27	250	4,850	438	3,750	1,500	109	453	7,140						
2/28	325	4,320	438	4,060	1,780	124	522	7,690						
Mean	145	3,970	463	3,820	1,730	104	428	7,390	2,410	2,240	170	3	3	0
Max.	325	6,430	625	6,880	2,550	135	522	10,400	2,740	2,530	210	4	4	0
Min.	25	2,580	375	2,810	1,300	75	370	5,320	1,840	1,660	130	2	3	0

All Results expressed in pounds per day

GLIDDEN COMPANY — U. S. PUBLIC HEALTH SERVICE

Data Summary Sheet

Source - Extracted Pyroligneous Acid Liquor

Date 1952	Immediate Oxygen Demand	B.O.D. 5 Day-20°C.	Color	pH	Acidity	Lignin and Tannin as Tannic Acid	Volatile Acids as Acetic Acid	Phenols	Ether Extractable Material	Oxygen Consumed	Solids					
											Total			Suspended		
											Total	Volatile	Fixed	Total	Volatile	Fixed
2/4	3,400	61,200	5,000	2.7	24,900 P 18,500 M	90,000	22,500	1,100	4,020	119,000	32,300	31,400	900	39	39	0
2/5	6,400	63,600	5,000	2.8	23,000 P 17,000 M	85,000	22,300	1,090	4,340	119,000	31,600	30,700	900	58	58	0
2/13	2,600	92,600	3,500	2.4	26,300 P 20,300 M	92,500	29,700	1,100	5,990	135,000	36,600	34,700	1,900	22	22	0
2/14	4,400	64,000	4,000	2.5	23,700 P 18,800 M	82,500	25,000	1,140	3,930	118,000	31,500	30,300	1,200	18	18	0
2/18	3,800	65,200	4,000	3.2	21,900 P 16,700 M	57,500	23,200	1,060	13,900	115,000	36,000	34,200	1,800	19	19	0
2/19	4,400	63,200	5,000	3.0	22,100 P 17,200 M	60,000	27,500	950	5,360	143,000						
2/20	5,400	60,600	5,000	2.9	23,600 P 18,600 M	55,000	22,300	1,090	8,240	128,000						
2/21	3,800	57,000	5,000	2.8	24,000 P 17,200 M	60,000	24,800	-	6,980	129,000						
2/25	3,800	69,000	5,000	2.8	23,100 P 17,000 M	60,000	24,500	1,080	7,180	123,000						
2/26	4,600	70,400	5,000	2.7	24,500 P 18,900 M	65,000	25,000	1,250	7,710	132,000						
2/27	4,800	73,600	4,000	2.7	23,200 P 17,600 M	60,000	23,600	1,260	11,100	124,000						
2/28	4,000	61,400	6,000	4.1	17,200 P 11,900 M	55,000	28,200	1,010	8,660	103,000						
Mean	4,280	66,880	4,700		23,100 P 17,600 M	68,500	24,900	1,100	7,270	124,000	33,600	32,300	1,300	31	31	0
Max.	6,400	92,600	6,000	4.1	26,300 P 20,300 M	92,500	29,700	1,260	13,900	143,000	36,600	34,700	1,900	58	58	0
Min.	2,600	57,000	3,500	2.4	17,200 P	55,000	22,300	950	3,930	103,000	31,600	30,300	900	18	18	0

P - Phenolphthalein
M - Methyl Orange

All results expressed in parts per million

CO-OPERATIVE INDUSTRIAL WASTE SURVEY

GLIDDEN COMPANY
NAVAL STORES DIVISION
JACKSONVILLE, FLORIDA

U. S. PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

Source - Extracted Pyroligneous Acid Liquor — Data Summary Sheet

Date 1952	Immediate Oxygen Demand	B.O.D. 5 Day-20°C.	Color	Lignin and Tannin as Tannic Acid	Volatile Acids as Acetic Acid	Phenols	Ether Extractable Material	Oxygen Consumed	Solids					
									Total			Suspended		
									Total	Volatile	Fixed	Total	Volatile	Fixed
2/4	425	7,660	625	11,300	2,810	139	503	14,900	4,040	3,930	110	4	4	0
2/5	800	7,960	625	10,600	2,790	136	583	14,900	3,950	3,840	110	7	7	0
2/13	325	11,600	438	11,600	3,710	138	749	16,900	4,580	4,340	240	3	3	0
2/14	550	8,010	500	10,300	3,130	143	492	13,800	3,940	3,790	150	2	2	0
2/18	475	8,160	500	7,190	2,900	133	1,740	14,400	4,500	4,280	220	2	2	0
2/19	550	7,910	625	7,510	3,440	119	670	17,900						
2/20	675	7,580	625	6,880	2,790	136	1,030	16,000						
2/21	475	7,130	625	7,510	3,100	-	863	16,100						
2/25	475	8,630	625	7,510	3,200	135	888	15,400						
2/26	575	8,810	625	8,130	3,130	156	964	16,500						
2/27	600	9,210	500	7,510	2,950	158	1,390	15,500						
2/28	500	7,680	750	6,886	3,530	126	1,080	12,900						
Mean	535	8,360	590	8,580	3,120	138	910	15,500	4,200	4,040	160	4	4	0
Max.	800	11,600	750	11,600	3,530	158	1,740	17,900	4,580	4,340	240	7	7	0
Min.	325	7,130	438	6,880	2,790	119	492	12,900	3,940	3,790	110	2	2	0

All results expressed in pounds per day

GLIDDEN COMPANY — U. S. PUBLIC HEALTH SERVICE

Source - Pyroligneous Acid Liquor from Final Waste Tank — Data Summary Sheet

Date 1952	Immediate Oxygen Demand	B.O.D. 5 Day-20°C.	Color	pH	Acidity	Lignin and Tannin as Tannic Acid	Volatile Acids as Acetic Acid	Phenols	Ether Extractable Material	Oxygen Consumed	Solids					
											Total Solids			Suspended Solids		
											Total	Volatile	Fixed	Total	Volatile	Fixed
2/4	3,880	63,880	4,000	2.7	30,200 P 18,800 M	55,000	17,700	1,720	8,640	132,000	35,400	34,600	800	926	918	8
2/5	3,700	59,200	3,500	2.8	23,000 P 17,800 M	100,000	26,000	1,760	8,590	131,000	38,300	37,300	1,000	1,140	974	166
2/13	3,000	83,800	3,000	2.3	25,700 P 20,000 M	100,000	25,800	2,870	20,200	193,000	54,800	53,100	1,700	972	972	0
2/14	1,400	86,800	3,500	2.5	24,300 P 19,200 M	105,000	23,500	2,180	17,600	156,000	21,700	21,200	500	1,720	1,710	10
2/18	4,200	57,800	4,000	3.2	22,000 P 16,800 M	75,000	23,300	1,910	22,500	133,000	47,500	42,500	5,000	1,480	1,480	0
2/19	1,600	33,600	5,000	3.0	22,200 P 17,200 M	30,000	23,500	1,600	30,700	131,000						
2/20	2,400	70,800	4,000	2.9	23,800 P 18,600 M	57,500	24,000	1,430	14,900	130,000						
2/21	4,800	58,800	3,500	2.7	24,000 P 17,600 M	60,000	23,400	-	13,500	126,000						
2/25	4,800	70,800	4,000	2.8	22,200 P 17,500 M	72,500	24,800	1,980	42,900	128,000						
2/26	4,600	10,200	4,000	2.7	25,200 P 17,400 M	72,500	27,200	1,940	20,200	150,000						
2/27	5,000	72,400	4,000	2.7	23,200 P 18,100 M	67,500	22,700	2,230	43,300	145,000						
2/28	4,200	64,800	5,000	4.1	17,200 P 11,900 M	60,000	24,600	2,110	23,800	127,000						
Mean	3,620	66,100	4,000		23,600 P 17,600 M	71,200	23,900	1,980	22,200	140,000	39,500	37,700	1,800	1,250	1,210	40
Max.	5,000	86,800	5,000	4.1	30,200 P 20,000 M	105,000	27,200	2,870	43,300	193,000	54,800	53,100	5,000	1,720	1,710	166
Min.	1,400	33,600	3,000	2.3	17,200 P 11,900 M	30,000	17,700	1,430	8,590	126,000	21,700	21,200	500	926	918	0

P - Phenolphthalein
M - Methyl Orange

All results expressed in parts per million

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CO-OPERATIVE INDUSTRIAL WASTE SURVEY

GLIDDEN COMPANY
NAVAL STORES DIVISION
JACKSONVILLE, FLORIDA

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ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

Source - Pyroligneous Acid Liquor from Final Waste Tank — Data Summary Sheet

Date 1952	Immediate Oxygen Demand	B.O.D. 5 Day-20°C.	Color	Lignin and Tannin as Tannic Acid	Volatile Acids as Acetic Acid	Phenols	Ether Extractable Material	Oxygen Consumed	Solids					
									Total			Suspended		
									Total	Volatile	Fixed	Total	Volatile	Fixed
2/4	475	7,980	500	6,880	2,210	215	1,080	16,500	4,430	4,430	100	116	115	1
2/5	463	7,400	438	12,500	3,250	220	1,070	16,400	4,790	4,670	120	143	121	22
2/13	375	10,500	375	12,500	3,230	359	2,530	24,100	6,850	6,640	210	122	122	0
2/14	175	10,900	438	13,100	2,940	273	2,200	19,500	2,710	2,650	60	215	214	1
2/18	525	7,230	500	9,380	2,910	239	2,810	16,600	5,940	5,320	620	185	185	0
2/19	200	4,200	625	3,750	2,940	200	3,840	16,400						
2/20	300	8,860	500	7,190	3,000	179	1,860	16,300						
2/21	600	7,360	438	7,510	2,930	-	1,690	15,800						
2/25	600	8,860	500	9,070	3,100	248	5,370	16,000						
2/26	575	8,780	500	9,070	3,400	243	2,530	18,800						
2/27	625	9,060	500	8,440	2,840	279	5,420	18,100						
2/28	525	8,110	625	7,510	3,080	264	2,980	15,900						
Mean	453	8,270	495	8,910	2,998	247	2,780	17,500	4,940	4,720	220	156	151	5
Max.	625	10,900	625	13,100	3,400	359	5,420	24,100	6,850	6,640	620	215	214	22
Min.	175	4,200	375	3,750	2,210	179	1,070	15,800	2,710	2,650	60	116	115	0

All results expressed in pounds per day

CO-OPERATIVE INDUSTRIAL WASTE SURVEY

GLIDDEN COMPANY
NAVAL STORES DIVISION
JACKSONVILLE, FLORIDA

AND

U. S. PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

Source - Retort Condenser Cooling Water					Data Summary Sheet		
Date 1952	Discharge M.G.D.	B.O.D. 5 Day-20°C. ppm	Color ppm	pH	Alkalinity ppm	Sulfides as S ppm	Phenols ppm
2/13	2.22	0.5	10	8.4	139 M	-	< 0.01
2/14	2.22	0.3	5	8.4	137 M	0.1	< 0.01
2/18	2.22	0.2	5	7.9	141 M	0.1	< 0.01
2/19	2.22	50	80	7.2	124 M	< 0.1	-
2/20	2.22	22	50	7.5	133 M	< 0.1	-
2/21	2.22	3.4	5	8.0	147 M	0.1	-
2/25	2.22	80	150	7.4	287 M	< 0.1	-
2/26	2.22	2.0	5	7.9	145 M	< 0.1	-
2/27	2.22	94	100	7.1	128 M	0.1	-
2/28	2.22	2.9	10	7.9	144 M	0.2	-
Mean	2.22	25.5	42		152 M	< 0.1	< 0.01
Maximum	2.22	94	150	8.4	287 M	0.2	-
Minimum	2.22	0.2	5	7.1	124 M	< 0.1	-

M - Methyl Orange

CO-OPERATIVE INDUSTRIAL WASTE SURVEY

GLIDDEN COMPANY
NAVAL STORES DIVISION
JACKSONVILLE, FLORIDA

U. S. PUBLIC HEALTH SERVICE
ENVIRONMENTAL HEALTH CENTER
CINCINNATI, OHIO

Source - Retort Condenser Cooling Water — Data Summary Sheet

Date 1952	Discharge M.G.D.	B.O.D. 5 Day-20°C Lbs/Day	Color Lbs/Day	Sulfides as S Lbs/Day	Phenols Lbs/Day
2/13	2.22	9	185	-	< 0.2
2/14	2.22	6	92	2	< 0.2
2/18	2.22	4	92	2	< 0.2
2/19	2.22	925	1,480	< 2	-
2/20	2.22	407	925	< 2	-
2/21	2.22	63	92	2	-
2/25	2.22	1,480	2,780	< 2	-
2/26	2.22	37	92	< 2	-
2/27	2.22	1,780	1,850	2	-
2/28	2.22	54	185	4	-
Mean	2.22	472	777	< 2	< 0.2
Maximum	2.22	1,780	2,780	4	< 0.2
Minimum	2.22	4	92	< 2	< 0.2

MODIFIED ANALYTICAL PROCEDURES

PHENOLS

Preliminary Screening Procedure

Add 2 ml. of 10 per cent copper sulfate solution to 250 ml. of sample and bring the pH of the mixture below 4.0 by the addition of 10 per cent phosphoric acid solution. Put the mixture in an all-glass distillation apparatus and distill over approximately 200 ml. Halt the distillation and allow the distilling flask to cool until boiling ceases. Add 50 ml. distilled water to the distilling flask and resume the distillation until a total of 250 ml. plus the volume of reagents added has been distilled over.

Acidify the distillate with 1 ml. of 10 per cent phosphoric acid solution and add 5 ml. of 10 per cent copper sulfate solution. Transfer the mixture to a separatory funnel containing 75 gm. fine-grained C. P. sodium chloride. Make three serial extractions with C. P. chloroform. On the first extraction, shake the mixture until the salt has been completely dissolved. Use 50 ml. of chloroform per extraction. Collect the chloroform extracts, discarding the aqueous phase after the third extraction. Combine the chloroform extracts. Extract the chloroform twice with 75 ml. portions of 0.1 N sodium hydroxide, discarding the extracted chloroform. Combine the alkaline extracts and make up to 250 ml. with distilled water.

Estimation of Phenols

Bromination Procedure

For phenol concentrations over 10 p.p.m.

Take an aliquot portion of the sodium hydroxide extract obtained in the screening procedure (the portion so taken that it contains about 0.05 gm.

phenols) and dilute to exactly 200 ml. Place the sample in a 500 ml. glass-stoppered Erlenmeyer flask and add 50 ml. of bromate-bromide solution (2.784 gm. $KBrO_3$ + 10 gm. KBr diluted to one liter with distilled water), followed by 5 ml. of concentrated hydrochloric acid. Place in hot water bath at 25°C. for one hour and add 2 gm. potassium iodide. After 5 minutes, titrate the liberated iodine with 0.1 N thiosulfate solution in the presence of starch indicator. Run a blank in the same manner using distilled water as the sample.

Calculation of Phenol

1 ml. 0.1 N thiosulfate solution = 0.001567 gm. phenol

$$\text{p.p.m. phenol} = \frac{[(\text{ml. thiosulfate for blank} - \text{ml. for sample})(1.567)(1,000)]}{\text{ml. of sample}}$$

Gibbs Procedure

For phenol concentrations less than 10 p.p.m.

Use the method in "Standard Methods for the Examination of Water and Sewage" (3). The dye produced by the Gibbs reaction was extracted with 5 ml. n-butyl alcohol from the aqueous phase and visual color comparison made in the top of Nessler tubes. The standard phenol solution was made from C.P. phenol alone, rather than a mixture of phenol and o-cresol.

DICHROMATE REFLUX METHOD FOR DETERMINATION OF OXYGEN CONSUMED

Special Apparatus

1. Reflux apparatus, consisting of 300 ml., round-bottomed flask with a 24/40 taper-joint neck connected with a Friedrich's reflux condenser.

Reagents and Solutions

1. Potassium dichromate, 0.2500 N
2. Sulfuric acid, concentrated
3. Ferrous ammonium sulfate, 0.2500 N
4. Indicator, o-phenanthroline ferrous complex

Procedure

1. Dilute an appropriate amount of sample to 50 ml.with distilled water in a 300 ml. round-bottomed flask with a taper joint neck.
2. Add 25 ml. of 0.2500 N potassium dichromate and 75 ml. of concentrated sulfuric acid. For the best quantitative results, use 50 per cent by volume sulfuric acid.
3. Reflux for two hours.
4. Cool, transfer the mixture to an Erlenmeyer flask and titrate the excess potassium dichromate with approximately 0.2500 N ferrous ammonium sulfate, using o-phenanthroline ferrous complex as an indicator.
5. Reflux a blank at the same time, using the same amount of reagents and substituting 50 ml. of distilled water for the sample.
6. The ferrous ammonium sulfate must be standardized daily.

Calculations

$$\text{O.C., p.p.m.} = \frac{(a-b) \times \text{normality (standard Fe)} \times 8000}{\text{Volume of Sample}}$$

where, O.C. = Oxygen Consumed

a = ml. of ferrous ammonium sulfate used for blank

b = ml. of ferrous ammonium sulfate used for sample.

DETERMINATION OF OIL (ETHER-EXTRACTABLE MATERIAL)

Sampling Procedure

1. Sampling Vessels

   (1) The sampling vessel shall be a clean glass-stoppered vessel of known capacity of approximately 1 liter.

   (1-a) If it is desired to examine composite samples, vessels shall consist of clean glass-stoppered vessels of known capacity. The total volume held by the number of portions composited shall be approximately 1 liter.

2. Extraction mixture, 50% C.P., fat-free, carbon tetrachloride by volume, 50% C.P. A.C.S. diethyl ether by volume.

3. Sample portions shall consist of a full bottle, or a vessel filled up to a prefixed calibration mark. The entire contents of a sample vessel must be used.

Procedure

Determine the pH of the sample. If compositing is being practiced, the subsamples should be composited in a 2-liter separatory funnel and mixed before the pH is determined. If the pH is above 6.0, add 1 ml. portions of concentrated HCl acid until the pH

falls below 6.0. Then, add a further 10 ml. portion of concentrated HCl acid. If the pH of the sample is initially below 6.0, add 10 ml. of concentrated HCl acid without preliminary adjustment of pH.

Rinse the sample container, or containers, with an 80 ml. portion of the extraction mixture. After the extraction mixture has been used to rinse the sample containers, transfer it to the extraction flask and shake vigorously for two minutes. The sample is allowed to stand long enough for the solvent layer to separate. The lower solvent layer is then separated. Rinse the sample container, or containers, with a further 60 ml. portion of solvent. Add the solvent to the sample in the separatory funnel and shake for two minutes. Separate the solvent layer and add it to the solvent already collected from the first extraction. Make a third rinsing and extraction, using a further 60 ml. portion and the same technique as was used for the second extraction.

Put the combined extract portions into the separatory funnel with 1 liter of distilled water and shake thoroughly for two minutes. Separate the extract, and wash the distilled water with 30 ml. of extraction mixture. Add the wash solvent to the separated extract. Filter the combined extract portions through a fat-free filter paper. Wash the paper three times with 5 ml. portions of solvent combining the filtrate and the wash solvent. Evaporate the combined extract on a steam bath under a hood in a weighed dish. When the solvent has been evaporated off, transfer the dish to an oven maintained at 103°C. Dry

for 30 minutes, cool the dish in a desiccator. Reweigh the dish.

Calculations

$$\text{Ether-Extractable Material, p.p.m.} = \frac{\text{Weight of extract in mg.}}{\text{Volume of sample in liters}}$$